consisted of the formation of a P–N sigma bond in which an electron pair from nitrogen would be donated to phosphorus. If such is the case, the above complexes would be the first examples in which tricoördinated phosphorus is acting directly as an acceptor in sigma bond formation.

Experimental

Materials.—The purification of trimethylamine and phosphorus trichloride was described in a previous paper.[1]

Both trimethylphosphine[5] and trimethylarsine[4] are from samples used in previous work and whose purification is therein described. The samples were refractionated in the vacuum line and vapor pressures determined. Trimethylphosphine had a vapor pressure of 159.1 mm. at 0°; trimethylarsine 99.6 mm. at 0°.

Phosphorus tribromide (Eastman Kodak) supplied in a sealed glass ampoule exhibited a vapor pressure of 1.0 mm. at 0°.

Procedures.—The vacuum techniques and reaction section used are the same as those reported previously.[1] All of the components could be measured out in the line except phosphorus tribromide. Sample sizes of the latter were obtained by direct weighing in the reaction ampoule flushed with nitrogen. Dry box techniques were employed for all transfer operations in which it was involved.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF ARGONNE NATIONAL LABORATORY, LEMONT, ILLINOIS]

Kinetics of the Reduction of Neptunium(VI) by Uranium(IV)[1]

BY J. C. SULLIVAN, A. J. ZIELEN AND J. C. HINDMAN

RECEIVED FEBRUARY 4, 1960

The kinetics of the reaction 2 Np(VI) + U(IV) = 2 Np(V) + U(VI) were studied in aqueous perchloric acid solutions and found to follow the rate law: $d[NpO_2^+]/dt = 2\,k[U^{+4}][NpO_2^{+2}]/[H^+]$. At an ionic strength of 2.00 and 25° the thermodynamic quantities of activation for the complex $(UOH\cdot NpO_2)^{+5}$ were found to be: $\Delta F^* = 16.05 \pm 0.01$ kcal./mole, $\Delta H^* = 18.2 \pm 0.2$ kcal./mole and $\Delta S^* = 7.4 \pm 0.8$ e.u. The effect of deuterium, ionic strength and the charge of the cations used to maintain the ionic strength were determined. The kinetics of analogous reactions of the (IV) and (VI) states of uranium, neptunium and plutonium are discussed.

Introduction

The various possible combinations in the reaction of the (IV) and (VI) states of uranium, neptunium and plutonium are all formally similar in that a quadrivalent ion is oxidized by a MO_2^{+2} ion, and it would therefore appear reasonable to predict a corresponding similarity in the kinetics of the reactions. However, this has not been found to be the case. Quantitative kinetic studies of the Np(IV)–Np(VI)[2] and U(IV)–Pu(VI)[3] reactions have yielded rate laws and postulated mechanisms of different forms, and a third type of rate law for the Pu(IV)–Pu(VI) and U(IV)–U(VI) reactions can be deduced from the disproportionation kinetics of the respective (V) states.[3–5] Thus a kinetic study of the U(IV)–Np(VI) reaction should extend our understanding of this system of reactions.

Experimental

The preparation and standardization of the following stock solutions have been previously described: neptunium (V) and (VI)[6]; perchloric acid, sodium perchlorate and thorium perchlorate[7]; deuterioperchloric acid[8]; and lithium perchlorate.[9] Reagent grade magnesium carbonate, lanthanum oxide and yttrium oxide were treated with perchloric acid followed by recrystallization to obtain the respective perchlorate solutions. Conventional procedures were employed by the analytical division of this Laboratory to standardize these solutions.

For the early experiments pure stock solutions of uranium (IV) perchlorate were prepared by dissolution of uranium trioxide in excess perchloric acid followed by electrolytic reduction with a continuous control potentiostat. However, it was later found more convenient to prepare the solutions by addition of excess granular lead to uranyl perchlorate in 2 molar perchloric acid. The reduction to uranium (IV) is quantitative and rapid, and solutions so prepared remained stable in U(IV) content for many weeks. The small amount of Pb^{+2} introduced in the stock solutions was found to have no detectable effect on the kinetics of the U(IV)–Np(VI) reaction. The uranium(IV) content was determined by addition of excess standard ceric perchlorate and titration with standard ferrous perchlorate to the ferroin end-point. Periodic checks of the stock solutions were also made spectrophotometrically at the 6480 Å. uranium(IV) absorption peak.

The reaction vessels were 5 cm. silica absorption cells, jacketed to allow continuous flow of water thermostated at the desired temperature. Stock solution aliquots of neptunium(VI), perchloric acid and sodium perchlorate (or other added salts) were added at room temperature. The cells were then placed in a Cary Model 14 MR Recording Spectrophotometer, the compartment of which was also independently thermostated at the working temperature. After attainment of temperature equilibrium an aliquot of uranium (IV) stock solution—maintained in a water-bath at the reaction temperature—was quickly squirted into the absorption cell by means of a micro pipet. The course of the reaction was followed by monitoring the growth of the 9800 Å. neptunium (V) absorption peak.

In the absence of added salts intitial concentrations of neptunium(VI) were obtained by radiometric assay of the reaction cell solutions; in all other cases initial concentrations were calculated from the stock solution concentration. Similarly hydrogen ion concentrations were determined by direct micro titration of the cell solutions whenever possible. In nearly all of the experiments neptunium(VI) was present in excess, and this, combined with the excellent stoichiometry observed in the reaction, allowed determination of the initial uranium(IV) concentration from the limiting optical density of each kinetic run. This procedure eliminated any errors due to air oxidation loss of uranium(IV) in transfer.

All concentrations were corrected for changes in solution volume with temperature and are reported in terms of moles/l. representated by the symbol M or by brackets.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. C. Hindman, J. C. Sullivan and D. Cohen, THIS JOURNAL, **81**, 2316 (1959); **79**, 4029 (1957); **76**, 3278 (1954).

[3] T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

[4] S. W. Rabideau, THIS JOURNAL, **79**, 6350 (1957).

[5] D. M. H. Kern and E. F. Orlemann, *ibid.*, **71**, 2102 (1949); H. G. Heal and J. G. N. Thomas, *Trans. Faraday Soc.*, **45**, 11 (1949).

[6] D. Cohen and J. C. Hindman, THIS JOURNAL, **74**, 4679 (1952).

[7] A. J. Zielen, *ibid.*, **81**, 5022 (1959).

[8] J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, **79**, 3672 (1957).

[9] A. J. Zielen and R. E. Connick, *ibid.*, **78**, 5785 (1956).

Results

The U(IV) and Np(VI) Dependencies.—Preliminary experiments indicated that in all cases when the initial concentration ratio [Np(VI)]/[U(IV)] > 2, the stoichiometry of the reaction corresponds to

$$2Np(VI) + U(IV) = 2Np(V) + U(VI) \qquad (1)$$

In the presence of excess U(IV) the Np(V) concentration increases to a maximum in accord with the above stoichiometry and then decreases slowly, undoubtedly due to the slow reduction of Np(V) by U(IV). On this basis it was assumed that the concentration of U(IV) at any instant could be calculated from the initial concentration and the amount of Np(V) formed.

Conventional use of the integrated form of the bi-molecular rate equation indicated the reaction to be first order in both U(IV) and Np(VI). Letting x equal the concentration of Np(V) formed at any time t and A and B the respective initial concentrations of Np(VI) and U(IV), linear plots were obtained with the function

$$(A/2 - B)^{-1} \ln \frac{B(A - x)}{A(B - x/2)} = \alpha + k't \qquad (2)$$

where k' is the apparent second order rate constant as defined by $d[NP(V)]/dt = k'[U(IV)][Np(VI)]$.

The presence of the α parameter in equation 2 allows the best fit to the data without the unnecessary restriction of a zero intercept. Indeed such treatment is desirable since errors in the true zero time and/or accelerated reaction speed due to high local concentrations before complete mixing of the reactants will yield rate data with an apparent intercept, but the true value of the rate constant is still obtained from the slope of the best straight line through the observed points. The α values observed in this research were generally small with standard deviations close to 100% and randomly positive or negative. Similar non-zero intercepts, but of a much greater magnitude and always positive, were reported in the study of the kinetics of the U(IV)-Tl(III) reaction by Harkness and Halpern.[10]

Actual treatment of the data was accomplished by weighted least squares calculations using an IBM 704 computer.[11] For these calculations equation 2 was recast in a form to allow input data in terms of observed optical densities and appropriate molar extinction coefficients. There is no interference by uranyl ion at the 9800 Å. Np(V) peak, but small corrections (1% or less) were applied for absorption by U(IV). The Np(V) molar extinction coefficient increases somewhat with both decreasing hydrogen ion concentration and temperature. Molar extinction coefficients appropriate for the solutions employed were determined from pure stock solutions of Np(V); values used covered the range 387 to 409.

Analysis of the kinetic data by the above procedure produced very good straight lines extending to 90% or better of completion of reaction 1, and deviations here could readily be accounted for in terms of the magnified effect of small errors in the initial concentrations. The least squares standard deviations of the slopes and hence k' usually were less than 1%. However, the fixed errors engendered by the $A/2 - B$ term in equation 2 increased the uncertainty in the rate constant for any one experiment to about 3-5%.

A final check on the metal ion dependences was made by investigating the possibility of back reactions involving the final products NpO_2^+ and UO_2^{+2}. Independent experiments with relatively high initial concentrations of these reaction products produced no observable effect on the kinetics. To determine the possible effect of UO_2^{+2}, a 12 fold excess over the amount formed was added and 4 fold for NpO_2^+. In the latter case the high initial NpO_2^+ concentration necessitated the use of the 6480 Å. U(IV) absorption peak to follow the reaction kinetics.

Effect of Hydrogen Ion, Temperature and Deuterium.—The simple bi-molecular kinetics observed with respect to the metal ions furnished the expected results, differences in the rate laws of the analogous reactions occur only in the hydrogen ion dependence.[2,3] Accordingly kinetic runs were carried out over the widest feasible acidity range with sodium perchlorate added to maintain the ionic strength at 2.00. Decreasing the reaction temperature successively to 15 and 5° allowed extension of the hydrogen ion range and also supplied the necessary data for determining the activation energy.

Correcting for the hydrolysis of U(IV), the observed rate law may be written in terms of the principal species in solution as

$$d[NpO_2^+]/dt = k''[U^{+4}][NpO_2^{+2}] \qquad (3)$$

where $k'' = k'([H^+] + K)/[H^+]$ and K is the equilibrium hydrolysis constant for the formation of UOH^{+3}. The reported value of K at 25° and $\mu = 2$ is 2.36×10^{-2} mole/l.[12] Values of K at 15 and 5° were calculated assuming $\Delta H = 11.0$ kcal.[13,14]

Plots of log k'' *vs.* log [H$^+$] established the hydrogen ion order of the rate law. The results are illustrated in Fig. 1 with nearly all of the points representing the mean of two to four kinetic runs. Metal ion concentrations were varied over the ranges 0.4 to 1.3×10^{-3} M for Np(VI) and 1.3 to 3.6×10^{-4} M for U(IV). The straight lines have all been drawn with a slope of minus one and with intercepts corresponding to the mean values of the rate constant as defined by

$$d[NpO_2^+]/dt = 2k[U^{+4}][NpO_2^{+2}]/[H^+] \qquad (4)$$

Or in terms of the apparent second order rate constants

$$2k = k''[H^+] = k'([H^+] + K) \qquad (5)$$

The factor of two incorporated in the rate constant anticipates discussion of the reaction mechanism. The Arrhenius activation energy calculated from these data gave the least squares value $E = 18.8 \pm 0.2$ kcal./mole (95% confidence level).

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[10] A. C. Harkness and J. Halpern, THIS JOURNAL, **81**, 3526 (1959).

[11] We are indebted to Mr. B. S. Garbow of the Applied Mathematics Division for programming this calculation. Weighting was introduced merely because of the functional nature of equation 2; equal weight was assigned to each observed optical density value.

[12] K. A. Kraus and F. Nelson, THIS JOURNAL, **72**, 3901 (1950).

[13] K. A. Kraus and F. Nelson, *ibid.*, **77**, 3721 (1955).

[14] R. H. Betts, *Can. J. Chem.*, **33**, 1775 (1955).

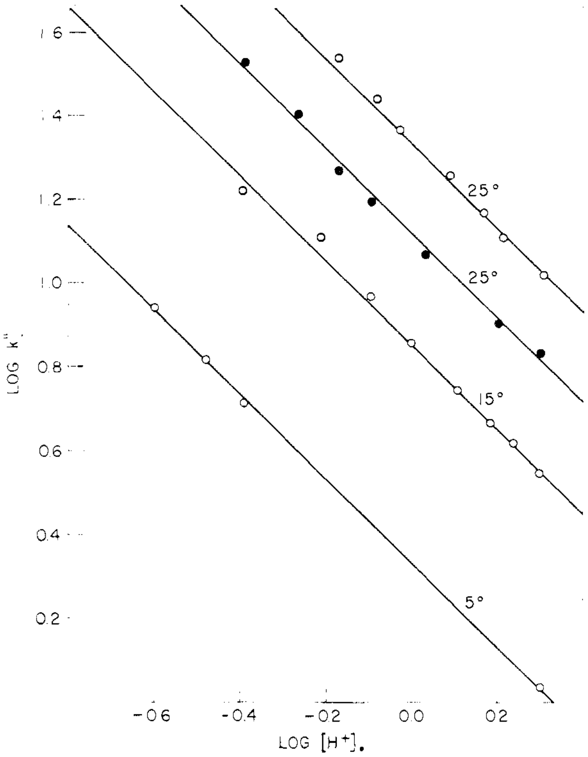

Fig. 1.—Hydrogen ion and temperature dependences of the apparent second order rate constant k'' at $\mu = 2.00$: ○, $NaClO_4$–$HClO_4$; ●, $NaClO_4$–$DClO_4$.

Figure 1 also contains the results obtained in deuterioperchloric acid and illustrates the considerable kinetic isotope effect. The appropriate value of K at 25° and $\mu = 2$ is reported to be 1.8×10^{-2} moles/l.[15]

A summary of the rate constant results is presented in Table I. The degree of consistency obtained using equations 4 and 5 is indicated by comparing the mean values of all results at varying $[H^+]$ with those obtained in 2 M perchloric acid (observed I and II, respectively). The best calculated values are also included and represent points on the least squares straight line obtained in the activation energy plot. All ± values are the statistical 95% confidence levels.

TABLE I

SUMMARY OF RATE CONSTANTS FOR $HClO_4$–$NaClO_4$ SOLUTIONS ($\mu = 2$)

Temp., °C.	$2k$, sec.$^{-1}$ Obsd., I[a]	Obsd., II[b]	Calcd.[c]
5	2.17 ± 0.03	2.17 ± 0.05	2.17 ± 0.04
15	7.16 ± .18	7.04 ± .15	7.07 ± .08
25	21.68 ± .43	21.35 ± .85	21.30 ± .39
25[d]	13.24 ± .32	13.67 ± .64	....

[a] Mean of all values at varying $[H^+]$. [b] Results in 2 M $HClO_4$. [c] From activation energy plot, 2 M acid data only. [d] Results in D_2O (*ca.* 95% D).

Equation 4 indicates the formula of the activated complex to be $(UOH{\cdot}NpO_2{}^{+5})^*$ but does not differentiate between the possible U(IV) species as the actual reactant. However, following the convention of Newton and Rabideau[16] in summarizing data of this type, the activation process is represented in terms of the principal species in solution

$$U^{+4} + NpO_2{}^{+2} + H_2O \rightleftharpoons (UOH{\cdot}NpO_2{}^{+5})^* + H^+ \quad (6)$$

It should be emphasized that equation 6 is not intended to imply details of the reaction mechanism. The thermodynamic quantities of activation corresponding to reaction 6 were calculated in the customary manner from the equation of absolute reaction rate theory.[17] The results at 25° and $\mu = 2$ at the 95% confidence level were: $\Delta F^* = 16.05 \pm 0.01$ kcal./mole, $\Delta H^* = 18.2 \pm 0.2$ kcal./mole and $\Delta S^* = 7.4 \pm 0.8$ e.u.

Ionic Strength and Medium Effects.—Values of the rate constant at different ionic strengths were determined by a series of experiments at 5° in perchloric acid solutions without added salts. The results are summarized in Table II. The appropriate values of the hydrolysis constant K were obtained by interpolation or extrapolation of the 25° data of Kraus and Nelson[12] and correction to 5°, again using $\Delta H = 11.0$ kcal.[13,14] Each listed value of the rate constant represents the mean of two to four kinetic runs.

TABLE II

VARIATION OF THE RATE CONSTANT WITH IONIC STRENGTH AT 5°

$[H^+]$, mole/l.	μ	$K \times 10^2$, mole/l.	$2k$, sec.$^{-1}$
0.1191	0.1243	1.43	1.15
1.075	1.080	0.72	1.47
2.001	2.006	0.62	2.17

Another series of experiments tested the effects of replacing the sodium perchlorate with various salts. Perchlorates of different valence types were selected to examine whether maintenance of constant ionic strength or constant total perchlorate ion was of more importance. All measurements were made at 15° in molar perchloric acid. Table III summarizes the results. The values of K were obtained in the same manner as indicated for Table II.

TABLE III

EFFECTS OF VARIOUS PERCHLORATE SALTS ON THE RATE CONSTANT; $[HClO_4]$, 1.00 M; t, 15°

Salt	μ	$[ClO_4^-]$, mole/l.	$K \times 10^2$, mole/l.	$2k$, sec.$^{-1}$
Na^+	1.99	1.99	1.24	7.21
Li^+	1.99	1.99	1.24	5.82
Mg^{+2}	2.00	1.67	1.24	6.08
	2.50	2.00	1.17	6.76
La^{+3}	2.00	1.50	1.24	8.96[a]
Y^{+3}	2.00	1.50	1.24	4.49
	2.99	2.00	1.11	5.08
Th^{+4}	2.00	1.40	1.24	5.40
	3.49	2.00	1.07	7.22

[a] Suspect value, trace of sulfate found in $La(ClO_4)_3$ stock solution.

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[15] J. C. Sullivan and J. C. Hindman, *J. Phys. Chem.*, **63**, 1332 (1959).

[16] T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

[17] S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 195–199.

The very low concentrations of reactant ions necessarily employed increased the customary difficulty of obtaining sufficiently pure salt solutions with minimal catalytic impurity effects. Newton[18] has demonstrated the accelerating effects of small amounts of sulfate in the kinetics of the U(IV)—Pu(IV) reaction, and similar observations were made in this study. Lithium perchlorate was first prepared by addition of perchloric acid to the best C.p. grade carbonate available. Kinetic runs using this stock, which was subsequently found to contain trace amounts of sulfate, gave $2k = 13.5$ sec.$^{-1}$. An additional purification procedure[9] removed the traces of sulfate and reduced the observed rate constant to the 5.82 sec.$^{-1}$ value listed in Table III. Traces of sulfate were also detected in the lanthanum stock solution, and the rate constant listed is undoubtedly too large. All other stock solutions tested free of sulfate and also of chloride. The data in Table III point out the rather substantial changes that may be produced in values of the apparent rate constant by varying the solution composition for this particular reaction. These results do not provide unambiguous evidence on the role of the perchlorate ion in this reaction in contradistinction to the observations previously presented on the Np(V)-Np(VI) isotopic exchange reaction[9] where a similar set of experiments rather conclusively ruled out the participation of the perchlorate ion in either an equilibrium preceeding the rate determining step or in the activated complex.

The difference in the apparent rate constant when *ca.* 1 *M* $LiClO_4$ is substituted for *ca.* 1 *M* $NaClO_4$ serves to emphasize the uncertainties inherent in the interpretation of the hydrogen ion dependence of this class of oxidation-reduction reactions in terms of other than a major path.[16]

Discussion

The empirically derived rate law is in accord with the mechanism

$$U^{+4} + H_2O \overset{K}{\rightleftharpoons} UOH^{+3} + H^+ \qquad (7)$$

$$UOH^{+3} + NpO_2^{+2} \xrightarrow{k_8} NpO_2^+ + U(V) \qquad (8)$$

$$U(V) + NpO_2^{+2} \xrightarrow{k_{9a}} NpO_2^+ + UO_2^{+2} \qquad (9a)$$

$$U(V) + U(V) \xrightarrow{k_{9b}} U(IV) + UO_2^{+2} \qquad (9b)$$

Reaction 8 is considered rate determining followed by fast reactions 9a or 9b. Either of reactions 9 will produce the observed stoichiometry and rate law, but as pointed out by Newton[3] for the analogous U(IV)-Pu(VI) reaction, both cannot be of importance since the resulting over-all rate law would not be first order in each of the metal ions. With U(V) presumably present as UO_2^+, reaction 9a is considered more likely since it involves a simple electron transfer. Assuming reaction 9a and making the conventional steady state assumption for the concentration of U(V), the derived rate law is identical to equation 4 with $k = Kk_8$. The choice between reactions 9 is not entirely trivial, since selection of 9b results in a rate equation without the factor of 2 contained in equation 4. This is a matter of some importance in calculating the correct ΔF^* and ΔS^* values for formation of the activated complex.[19]

Kinetic results now available on the (IV)-(VI) oxidation-reduction reactions of the actinides are summarized in Table IV. For comparative purposes both the form of the rate laws and the numerical values of the rate constants at 25° and $\mu = 2$ are listed. The observed rate constants are corrected for the hydrolysis of the respective (IV) states and correspond to the k'' of equation 3. Minor changes in the previously reported constants for the Np(IV)-Np(VI) reaction[2] resulted through the use of the hydrolysis correction; also expressing the results in terms of the appearance of the (V) state introduced another factor of two. The results presented for the Pu(IV)-Pu(VI) reaction are entirely hypothetical. The form of the rate law is deduced from the disproportionation kinetics of Pu(V).[4] The magnitude of the rate constant is calculated from the disporportionation rate constant and the equilibrium quotient for the over-all reaction as calculated from the formal potentials of the pertinent plutonium couples.[20] An entirely similar picture is presented by the disproportionation kinetics of U(V).[5]

TABLE IV

SUMMARY OF KINETICS FOR (IV)-(VI) REACTION OF U, Np AND Pu

$t = 25°$; $\mu = 2$

$k'' = [MO_2^{+2}]^{-1}[N^{+4}]^{-1}d[MO_2^+]/dt$

Reaction	k'', (mole/l.)$^{-1}$ sec.$^{-1}$	Ref.
U(IV)-Np(VI)	$21.3/[H^+]$	[a]
U(IV)-Pu(VI)	$8.68/([H^+] + 0.385[H^+]^2)$	3
Np(IV)-Np(VI)	$0.0886/[H^+]^2 + 0.0080/[H^+]^3$	2
Pu(IV)-Pu(VI)	$3 \times 10^{-7}/[H^+]^3$	4, 20[b]

[a] This work. [b] Ionic strength = 1.

The reactions of Table IV run an interesting gamut both in hydrogen ion dependences and magnitude of the rate constants. In each case the potential barrier crossed can be represented by an activated complex of the general form $(M(OH)_n\cdot MO_2)^{+6-n}$ with n varying from 1 to 3. However, the factors determining the n value(s) for any particular reaction do not admit of rationalization based upon any model simple enough to be amenable to calculation.

The U(IV)-Np(VI) system clearly presents the simplest kinetic picture so far observed in reactions of this type and on this basis warrants a more detailed examination of the reaction mechanism. Equation 8 can be formally expanded in the form

$$UOH^{+3} + NpO_2^{+2} = (UOHONpO^{+5})^* \longrightarrow UO^{+3} + NpO_2H^{+2} \qquad (8a)$$

$$UO^{+3} + H_2O \longrightarrow UO_2^+ + 2H^+ \qquad (8b)$$

$$NpO_2H^{+2} \longrightarrow NpO_2^+ + H^+ \qquad (8c)$$

with the dismutation of the activated complex as the rate determining step.

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(18) T. W. Newton, *J. Phys. Chem.*, **63**, 1493 (1959).

(19) Selecting alternate reaction 9b, the change in the previously listed thermodynamic quantities of activation would be a 0.41 kcal. decrease in ΔF^* and the concomitant increase of 1.4 e.u. for ΔS^*.

(20) S. W. Rabideau, THIS JOURNAL, **78**, 2705 (1956).

The hydrogen atom transfer mechanism implied above is particularly attractive in that it furnishes a ready explanation of the role of hydrogen in the reaction and does not involve extensive rearrangement of the hydration shells of the reactants. Similar arguments have been advanced for many of the aqueous reactions of the actinides, and evidence for or against hydrogen atom transfer has been sought by determining the kinetic isotope effect produced by the substitution of deuterium.[16] However, interpretation of the results is generally ambiguous due to unknown effects of D_2O on solvation.[21]

For the present case the gross kinetic isotope effect at 25° is indicated from Table I to be $k_H/k_D = 1.61 \pm 0.05$. This value must be corrected for the deuterium effect on the prior hydrolysis equilibrium (equation 7). Using the hydrolysis quotient results previously determined,[15] we obtain the net corrected value $k_{8H}/k_{8D} = 1.4 \pm 0.1$. Although these results are consistent with the concept of a hydrogen atom transfer mechanism, heavy water effects of comparable magnitude have been observed in reactions that do not explicitly involve hydrogen or water,[21,22] hence the observations cannot be cited as unambiguous evidence for the proposed mechanism. Alternatively we may postulate a direct electron transfer mechanism with the product UOH^{+4} reacting rapidly to give UO_2^{+2} after the dismutation of the activated complex.

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[21] A. E. Ogard and H. Taube, THIS JOURNAL, **80**, 1084 (1958).

[22] S. W. Rabideau and R. J. Kline, *J. Phys. Chem.*, **62**, 617 (1958).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF ALABAMA, UNIVERSITY, ALABAMA]

The Equivalent Conductance of the Hexafluorocomplexes of Group IV (Si, Ge, Sn, Ti, Zr, Hf)[1]

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The limiting equivalent conductance values have been determined for the hexafluorocomplex ions of six elements in Group IV. The potassium, rubidium and cesium salts for each of the fluorocomplexes were prepared and used in determining the value. The plot Λ *vs.* $C^{1/2}$ yielded the curve of the typical weak electrolyte. However, when these values were corrected for the hydronium ion contribution, the plots yielded a straight line corresponding to the equation $\Lambda = \Lambda_0 - bC^{1/2}$.

The limiting equivalent conductance values for the hexafluorocomplex ions of silicon, germanium, tin, titanium, zirconium and hafnium were determined in aqueous solution. The potassium, rubidium and cesium salts of each of the above hexafluorocomplexes were prepared and purified, and their corrected equivalent conductance values were determined. The use of three salts for each of the hexafluorocomplexes served as a means of checking the quality of the procedure and the limiting equivalent conductance value determined.

Experimental

Apparatus and Method.—The basic equipment consisted of the Leeds and Northrup Jones conductance bridge, Hewett-Packard Audio Oscillator Model 200AB, the Kay Lab Twin-T rejection filter No. 503A placed between the bridge and detector and a Dumont 401 oscilloscope and ear phones as detectors. The conductance cells were of the design recommended by Jones and Bollinger.[3]

The constant temperature bath, in which paraffin oil was used as the liquid, was controlled with a Labline #3202 differential thermoregulator. Due to the properties of the paraffin oil, large temperature gradients were found in the bath when the usual knife-blade or resistance-coil heating elements were used. An infrared heating lamp placed above the bath produced very even heating. A kerosene–oil mixture at 14 ± 1° from an external refrigeration unit was circulated through the cooling coils of the bath. The temperature of this bath, as measured with a Leeds and Northrup platinum resistance thermometer and a Mueller bridge assembly, both with National Bureau of Standards Certificates, was held at 25.00 ± 0.005° for several months.

The Leeds and Northrup *p*H Indicator Assembly was used for all *p*H measurements. After the *p*H of a given solution had been determined, it was closely bracketed with standard solutions as *p*H 4.20 and 4.40.

Materials.—Most of the hexafluorocomplex salts were prepared by adding the alkali halide to the hexafluorocomplex acid and precipitating the resulting hexafluorocomplex salt, filtering, washing and recrystallizing the salt several times. These compounds were prepared in platinum and/or polyethylene containers. De-ionized water was used in all steps. The prepared salts were examined spectrographically for impurities.

Hexafluorosilicates.—The cesium hexafluorosilicate was prepared by double decomposition of previously prepared cesium hexafluorostannate. The latter salt is about four times as soluble as the former.

Hexafluorogermanates.—Potassium hexafluorogermanate was prepared according to the method given by Brauer.[4] The rubidium and cesium salts were prepared in a similar manner except that rubidium fluoride was used instead of the chloride.

Hexafluorostannates.—The potassium hexafluorostannate was prepared by the method described by Marignac.[5] The rubidium and cesium salts were prepared by using alpha-stannic oxide. Calcium carbonate was added to concentrated stannic chloride solution until further addition produced no effervescence. The gelatinous white precipitate, alpha-stannic oxide, was thoroughly washed, then partially dissolved in 48% hydrochloric acid. After about 12 hr. the clear supernatant liquid, containing the hexafluorostannic acid, was siphoned off, concentrated and filtered. The fluorostannic acid was carefully added to solutions of rubidium chloride and cesium chloride till no further precipitation took place.

Hexafluorotitanate.—Very pure titanium dioxide, prepared according to Brauer,[6] was dissolved in excess hydrofluoric acid, and then the concentrated solution of alkali halide was

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[1] This research was supported by Air Force Office of Scientific Research, AF-18(600)-1567.

[2] (a) 14 Rue De La Paix, Schiltigheim, France. (b) Abstracted from the dissertation presented by Robert H. Schmitt in partial fulfillment of the requirements for the doctorate degree.

[3] G. Jones and G. M. Bollinger, THIS JOURNAL, **53**, 411 (1931).

[4] G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p. 544.

[5] J. C. Marignac, *Ann. Minnes.*, **15**, 221 (1859).

[6] G. Brauer, *ibid.*, p. 857.